25

ON THE STRUCTURE OF THE RESONANCE LINE OF Hg FILTERED THROUGH Hg VAPOUR*

By G. S. KASTHA

(*Received for publication, May 12, 1949*)

Plate VIII

ABSTRACT. The structure of the resonance line 2536.6 Å of mercury filtered through a cell containing mercury vapour at different temperatures and pressures has been studied with an Adam Hilger large (E_1) quartz spectrograph. It has been observed that the mercury vapour in the absorption cell absorbs only the central portion of the resonance line, there being a feeble line transmitted on each side of the centre. The distance between these two lines increases to about 18 cm^{-1} when the temperature of the mercury in the absorbing cell is raised to 100°C. The intensity of these two lines is much less than that of the line 2534.8A° and is of the same order of magnitude as that of the Brillouin components observed by Krishnan in the case of diamond. It is pointed out that as the separation and the intensity of those Brillouin components are the same as those of the doublet in the resonance line filtered through mercury vapour it is doubtful whether the lines observed by Krishnan are genuine Brillouin components in the light scattered by diamond.

INTRODUCTION

It has been pointed out recently by Krishnan (1947) that the line 2536.6 Å of mercury scattered by diamond and afterwards filtered through mercury vapour shows, when examined with either a medium or a high dispersion quartz spectrograph, a structure which consists of a doublet, the two components being separated from each other by about 12 cm^{-1}. Each of these components on more careful examination has been found to be composed of one intense inner component and another fainter outer component. This splitting of the scattered line has been explained by Krishnan on the hypothesis that Brillouin components are produced by sound waves of thermal origin moving in the crystal, the transverse and longitudinal waves giving rise to the inner and outer pair of the components respectively. He has calculated the relative intensities of the inner and outer components from the theory put forward by Leontowitsch and Mandelstam (1932) and has found that the observed values do not agree at all with those calculated from the theory. The theory predicts that the component due to the longitudinal waves should be more intense than that due to the transverse waves, but actually the reverse is fouud to be true.

* Communicated by Prof. S. C. Sirkar

There is another discrepancy also, which has not been explicitly pointed out by Krishnan. According to the theory mentioned above, the ratio of intensity of the component scattered by the transverse sound waves to that of the undisplaced component should be about 0.31×10^{-5}. The value of this ratio actually observed has not been calculated by him, but he has mentioned that the aggregate intensity of all the Doppler components is less than one fourth the intensity of the Raman line. From this the ratio of intensity of the component due to transverse waves to that of the Raman line can be taken as 1 : 6. The Rayleigh line, however, is not more than 1000 times as intense as the Raman line, because the 1332 cm^{-1} line excited by the Hg line 4046 Å is more intense than the Hg line 4140 Å and the 4046 Å line is not more than 10^3 times as intense as the line 4140 Å. Hence the ratio of the intensity of the Brillouin component due to transverse waves in diamond at room temperature to that of the undisplaced component is of the order of 10^{-4} while theoretically it should be of the order 10^{-6}. From these facts it appeared that the problem deserved more careful reinvestigation and the present investigation was undertaken with that object in view.

EXPERIMENTAL

In the preliminary investigation a small diamond transparent to Hg line 2536 6 Å was used for photographing its Raman spectrum excited by the resonance line with an Adam Hilger medium quartz spectrograph. A cell containing a few drops of mercury and provided with quartz windows was placed in the path of the scattered light to absorb the resonance line of mercury. A quartz lens was used to focus this light on the slit of the spectrograph. There was also an arrangement for raising the temperature of the cell at will with an electric heater. The Hg line 2536.6 Å scattered by the diamond and transmitted through mercury vapour was found to consist of a doublet, the two components being placed symmetrically on the two sides of the central core which was completely absorbed by the mercury vapour in the cell. Since the proportion of stray light was very great in the light focussed on the slit of the spectrograph and yet the central core of the line 2536.6 Å was absorbed by the vapour it was suspected that even the incident resonance line of mercury when filtered through mercury vapour might be split up into two components. In order to investigate this question the direct light from a quartz mercury arc with its cathode end immersed in running water was passed through the cell containing mercury vapour and the spectrum of the transmitted light was photographed with the quartz spectrograph mentioned above and also with a large Adam Hilger E_1 quartz spectrograph.

Several photographs of the spectrum were taken keeping the mercury vapour in the cell at different temperatures. The heating coil of the cell was wound so as to produce no magnetic lines of force and in order to ensure that the results obtained were not being affected by the residual magnetic

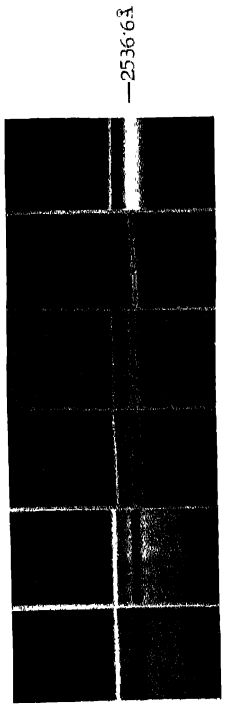

Fig 1 Unfiltered.

Fig 2 Absorbing vapour at 25°C

Fig 3 " " 55°C

Fig 4 " " 75°C

Fig. 5 " " 100°C

Fig. 6 " " 110°C

Resonance line of Hg filtered through Hg vapour.

field produced by the heating coil, another identical cell heated with a Bunsen burner was used and the resonance line transmitted by this cell was photographed. It was observed that the results obtained with the cell heated either electrically or with a burner were identical.

RESULTS AND DISCUSSION

The spectrograms obtained with absorbing mercury vapour at different temperatures are reproduced in Plate VIII. Fig. 1 shows the spectrum of the light from the mercury arc not filtered through any mercury vapour. Figs. 2, 3, 4 and 5 show the spectrograms with the absorbing vapour at 25°C, 55°C, 75°C and 100°C respectively. Fig. 4 also shows the spectrogram with the absorbing vapour heated by a Bunsen burner to 75°C. In the case of the spectrogram reproduced in Fig. 6 the temperature of the absorbing vapour was about 110°C.

It can be seen from these spectrograms that only the core of the 2536 6Å line is absorbed by the vapour in the cell while regions on both sides of the core are transmitted. When the vapour is at about 30°C the width of the absorbed central core is only 5 cm^{-1} and the intensity of each of the two bands appearing on the two sides of the central core is almost the same as that of the line 2534.8Å. As the temperature of the vapour is raised the intensity of the doublet goes on diminishing rapidly and at 100°C the intensity becomes only about one third that of the line 2534.8A°. It is also quite clear from the spectrograms in Plate I that the separation of the two components increases rapidly at higher temperatures. The values of the separation for different temperatures are given in Table I. The width of each component of the doublet remains almost constant with the rise of temperature of the absorbing vapour.

TABLE I

Temperature in degrees Kelvin.	Separation of the doublet in cm^{-1}	Width of each component in cm^{-1}
298	5.2	4.4
328	6.33	4.5
348	11.18	4.5
373	18.6	4.5
383	24.3	4.8

A careful examination of the spectrograms reveals that in the spectrogram due to the unfiltered light from the mercury arc the intensity at a distance of 8 cm^{-1} from the centre of the 2536.6 A° line is much too feeble to account for the appearance of the two components of the doublet at these positions

in the spectrogram due to the light filtered through mercury vapour at about 100°C. This can be clearly seen from figs. 1 and 5 in both of which the Hg line 2534.8 Å is almost of the same intensity, and although there is no blackening in Fig. 1 at 8 cm^{-1} from the centre of the line 2536.6 Å, a doublet appears at this position in Fig. 5.

A small percentage of light of changed wavelengths is thus created while in the line 2536.6 Å traverses the heated mercury vapour in the cell. It is also evident from Table I that the change in frequency increases very rapidly with the rise in temperature. This fact suggests that the observed change in the frequency of the light is not due to Döppler effect on Rayleigh scattering, because the velocity of the Hg atoms increases only in the ratio $\sqrt{\frac{373}{300}}$ when the vapour at 27°C is heated to 100°C, while the change in frequency increases four times. Further, the shift due to Döppler effect would be only about 0.1 cm^{-1}, while the shift actually observed is 9 cm^{-1}. Hence this effect is to be ascribed to some other property of the vapour.

In this connection it has to be pointed out that Lennuier (1947) observed an effect which might be considered to be a reverse phenomenon of what is observed in the present investigation. He studied the scattering of light of wavelength just in the neighbourhood of that of the resonance line of mercury by mercury vapour at a pressure of 1.84×10^{-4}mm. It was observed by him that although the 2536.6 Å line itself was not present in the incident light but light of slightly different wavelength was used as the incident light, the light scattered in the transverse direction contained a large proportion of light of wavelength 2536.6 Å. He explained this phenomenon on a theory of scattering of light by the mercury atoms in the neighbourhood of resonance frequency. Later, Lennuier (1948) reported that the phenomenon is observed with the incident light of frequency ν_1, when ν_1 is either greater than or less than ν_0, where ν_0 is the resonance frequency. In his experiment ν_1 differed from ν_0, by about 1 cm^{-1} only and the incident light of these frequencies was obtained by splitting the resonance line of mercury by applying a longitudinal magnetic field to the vapour emitting the line. In the present investigation in the process of scattering in the forward direction the value of ν_0 is observed to be changed by about 9 cm^{-1}. Hence although this process may be considered to be the reverse of that observed by Lennuier the magnitude of the change is much larger than that observed by him.

This broadening of the resonance line of mercury during absorption by mercury vapour in presence of foreign gases was observed indirectly from results of measurement of absorption by mercury vapour of the resonance line long ago by previous workers. Wood (1922) showed that when the resonance radiation from mercury vapour is filtered through a cell containing cold mercury vapour and the filtered light is allowed to illuminate mercury vapour in a second cell the intensity of the resonance radiation excited in

the latter cell is very small. If, however, helium is introduced as a foreign gas in the second cell the intensity of resonance mercury radiation increases enormously. This shows that ordinarily only the core of the resonance line can excite the resonance radiation in a second cell, but when foreign gas is introduced the excitation takes place even when the core has been absorbed in the incident light. Evidently, the presence of molecules or atoms of foreign gas broadens the resonance level of the mercury atom. Orthmann (1925) calculated theoretically the broadening of the absorption of the resonance line by mercury atoms in presence of hydrogen atoms and came to the conclusion that at a pressure of 253 mm. hydrogen atoms can increase the half width of the resonance line in absorption from its original value 1.01×10^{-3} Å to about 8.0×10^{-3} Å. The broadening of the resonance line observed in the present investigation is many times larger and cannot be explained by Orthmann's theory of collisional broadening. Although atmospheric nitrogen may have been present in the cell containing the mercury vapour which was used to absorb the resonance line in the present investigation and part of the broadening of the absorption line may be due to collisional effect the magnitude of the broadening actually observed is much larger than that predicted by Orthmann's theory. On the other hand, Oldenberg (1928) observed by spectroscopic examination that when helium at a pressure of one atmosphere is mixed with mercury vapour at low pressure in a resonance lamp a band extending from 2519 Å up to 2570 Å accompanies the 2536.6 Å line. Nitrogen at low pressure may therefore similarly widen the resonance line in the resonance tube to a smaller extent.

It appears from the results of the present investigation that not only the width of the resonance line in absorption increases with the rise of the temperature and consequently with the increase in the number of collisions, but fluorescence radiations of wavelengths differing only slightly from those of the edges of the absorption band are also emitted by the mercury atoms. The difference between the wavelengths of these radiations and that of the centre of the resonance radiation also increases with the temperatue of the vapour. In this connection it may not be irrelevant to point out that in the spectrograms published by Wood (1925) in figs. 5(*b*) and 5(*c*), Plate XXV, the resonance line 2536.6 Å seems to be unusually broad. He has mentioned that water vapour and nitrogen were present in the resonance tube in the former case and helium was present in the latter case and these foreign gases gave rise to some extra bands. The widening of the resonance line was not mentioned by him explicitly although the broadening extends up to a few Angstrom units. It is clear, however, from a comparison of the spectrograms reproduced by Wood and those obtained in the present investigation that the width of the resonance line in emission is always greater than that of the line in absorption. The feeble resonance radiation

of changed wavelength is therefore not absorbed by the mercury vapour through which it has to come out.

The intensity of the two components of the filtered resonance line observed in the present investigation is of the same order of magnitude as that of the Brillouin components observed by Krishnan (1947), as can be seen from a comparison of the intensity of these components with that of the line 2534.8 Å. The intensity of the two components is of the order of 1/10000th of the intensity of the line 2536.6 Å itself, because it is a little less than that of the Raman line 1332 cm^{-1} excited by the line 2536-6 Å. The separation of the two components is also of the same order of magnitude as that observed by Krishnan (1947). These facts and also the fact that the width of the absorption line is always less than that of the emission line lead to the conclusion that the doublet observed by Krishnan may not be Brillouin components, but they may due the broadening of the resonance line in the absorbing mercury vapour as discussed in this paper.

ACKNOWLEDGMENT

The author is indebted to Prof. S. C. Sirkar for his kind interest and guidance during the progress of this work.

INDIAN ASSOCIATION FOR THE
CULTIVATION OF SCIENCE,
CALCUTTA

REFERENCES

Krishnan, R. S., 1947, *Proc. Ind. Acad. Sci.*, **26A**, 399.
Leontowitsch, M. and Mandelstam, S., 1932, *Phys. Z. Sowjet*, **1**, 317.
Oldenbarg, O., 1928, *Z. f. Phys.*, **47**, 184.
Orthmann, W., 1925, *Ann der Phys.*, **78**, 601.
Wood, R. W., 1922, *Phil. Mag.*, **44**, 1107.
,, ,, 1925, *Phil. Mag.*, **50**, 774.